

On the possibility of clathrate hydrates on the Moon

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Abstract. One of the most important inferences of the Lunar Prospector mission data was the existence of subsurface water ice in the permanently shadowed craters near both lunar poles [Feldman *et al.*, 1998]. We propose and substantiate an alternative explanation that hydrogen can exist in the shallow lunar subsurface in the form of clathrate hydrates: $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ and/or $\text{CO}_2 \cdot 6\text{H}_2\text{O}$.

The Clementine mission in 1994 [Nozette *et al.*, 1994] was the first to suggest the possible existence of subsurface water ice near the poles of the Moon. The Lunar Prospector neutron spectrometer data showed near-surface deposits enriched in hydrogen near both lunar poles under at least 40 cm of lunar regolith (with the assumed density of 2 g/cm^3 [Feldman *et al.*, 1998]).

Scientists estimated that as much as 6 billion metric tons of water ice may be buried in these craters under lunar soil, in more concentrated deposits than originally thought. However, the evidence was indirect, they cautioned, based on reasonable scientific assumptions, given the levels of hydrogen detected, from which water ice was inferred. This conclusion was based on the measurements of the fast and epithermal neutrons by the neutron spectrometer reflected by lunar soil with the source being cosmic rays. We propose that the neutron spectrometer data are also consistent with the existence of clathrate hydrates I, e.g., $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ and/or $\text{CO}_2 \cdot 6\text{H}_2\text{O}$, in the shallow subsurface of the Moon. In clathrate hydrates the gas molecule is trapped in a cage by electrical van der Waals bonding.

The controlled crash of NASA's Lunar Prospector spacecraft into a crater near the south pole of the Moon on July 31, 1999, produced no observed signature of water, according to scientists analyzing the data from Earth-based observatories and spacecraft such as the Hubble Space Telescope. Although the chances of positive detection of water were judged to be <10%, worldwide observations of the impact were focused primarily on using sensitive spectrometers tuned to look for the ultraviolet emission lines expected from the hydroxyl (OH) molecules that should be a by-product of any icy rock and dust kicked up by the impact of the spacecraft. This lack of physical evidence leaves open the question of whether ancient cometary impacts delivered ice that remains buried in permanently shadowed regions of the Moon, as suggested by the large amounts of hydrogen measured indirectly from lunar orbit by Lunar Prospector during its main mapping mission [NASA, 1999].

Several possible explanations why any water signature was not detected include the following: the spacecraft might have missed the target area; the spacecraft might have hit a rock or dry soil at the target site; water molecules may have been firmly bound in rocks as a hydrated mineral as opposed to existing as

free ice crystals, and the impact lacked enough energy to separate water from hydrated minerals; no water exists in the crater, and the hydrogen detected by the Lunar Prospector spacecraft earlier is simply pure hydrogen; studies of the impact's physical outcome were inadequate; the parameters used to model the plume that resulted from the impact were inadequate; the telescopes used to observe the impact, which have very small fields of view, may not have been pointed correctly; and water and other materials may not have risen above the crater wall or otherwise were directed away from the telescopes' view [Barker *et al.*, 1999; NASA, 1999].

The study of terrestrial gas hydrates emerged not long ago [e.g., Holder and Bishnoi, 2000]. Initially, they were seen as impediments in gas pipelines. The first announcements about discoveries of CH_4 hydrate fields under the permafrost zone in Siberia were made in 1965 [e.g., Makogon, 1981; Sloan, 1998, p. 8]. In the gas, which evolves upon dissociation from the hydrate deposit under permafrost in Siberia (called Medvezh'e), CH_4 comprises ~98.1% (e.g., Tiptenko *et al.* [1990]; also see there a nonlinear numerical model for gas hydrates formation and dissociation). Similar high methane abundance is found in many other gas hydrate deposits on Earth. Later, gas hydrates were found in Canada and Alaska. The incentive for those studies was that methane clathrate hydrate is a valuable source of fuel and also presents a danger to those searching for oil and gas. Interestingly, discussions of possible occurrences of clathrate hydrates on different solar system bodies did not mention the Moon as a candidate.

According to the chemical analyses of numerous lunar samples from Apollo 11, 12, 14, 15, and 16 landing sites, trapped CH_4 gas is a ubiquitous component of these samples, including samples from different depths [see Pillinger *et al.*, 1977; Abell *et al.*, 1971; Cadogan *et al.*, 1971, 1972; and references therein]. The samples include the Apollo 12 double core, the Apollo 14 surface samples, and the Apollo 15 and 16 deep drill stems [Wszolek and Burlingame, 1973]. All of the evidence from the Apollo missions suggests that methane is formed on the Moon and is likely to be a lunar soil chemistry product from the solar wind implanted carbon and hydrogen [Pillinger *et al.*, 1977]. Recent work by Crider and Vondrak [2000] suggests that the solar wind origin is also possible for hydrogen deposits detected at the lunar poles (cold traps). However, over time there could have been additional sources of volatiles in the polar regions, such as comets, micrometeorites, and magnetospheric fluxes. Keeping this in mind, it is natural to check if the com-

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pound, which can be formed out of methane gas and water ice, is stable on the Moon.

The temperature in the polar, permanently shadowed craters was estimated to be <102 K [Igersoll *et al.*, 1992; Vasavada *et al.*, 1999, and references therein]. We have calculated the depth needed to stabilize the clathrates within permanently shadowed lunar craters. For the temperature $T = 100$ K, $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ is stable at the methane gas partial pressure $P \geq 2.1 \times 10^{-5}$ bars = 2.1 Pa = $P_{\text{stabilizing}}$ [Lunine and Stevenson, 1985; Berecz and Balla-Achs, 1983, p. 61; Makogon, 1981, p. 5; Miller, 1961, p. 1803]. Since the system is in equilibrium, this partial pressure should be equal to the lithostatic pressure of the impermeable “lid,” which could be water ice or permafrost (water ice in pores). The experiments by Wright *et al.* [1998] on methane hydrate formation and dissociation showed that (T, P) equilibrium conditions for hydrate stability in porous media are only slightly offset from values determined for pure-system hydrates.

We took the density of the “lid” $\rho = \rho_{\text{pure water ice}} = 900$ kg/m³ (the worst case scenario since the permafrost density is greater). The condition of the equilibrium with the upper water-ice seal is given by

$$P_{\text{stabilizing}} = P_{\text{CH}_4} = P_{\text{lithostatic}} = \rho gh,$$

where the lunar acceleration of gravity $g = 1.62$ m/s². This gives a depth of ~ 1.5 mm. Clathrate hydrates, moreover, can exist at greater depths in a shallow lunar subsurface, where the temperature does not increase significantly with depth. For a lunar internal heat flow of $\sim 22 \times 10^{-3}$ W/m² [Heiken *et al.*, 1991] and a thermal conductivity of ice at 100 K of ~ 1.76 W/mK, the temperature increases only by ~ 0.1 K at a depth of 8 m within the permanently shadowed craters. The lack of a fast-neutron signature [Feldman *et al.*, 1998] rules against surface hydrogen-rich layers.

The H₂O ice seal can form as a result of the upper clathrate dissociation (the effect of self-preservation; experiments by Ershov *et al.* [1991]; Sloan [1998, p. 19]). These experiments were performed with both CO₂ and CH₄ clathrate hydrates. The upper water-ice (or permafrost) seal makes the system closed and does not allow CH₄ molecules to diffuse into the near-vacuum conditions, as they would through the permeable lunar regolith.

In addition to a solar wind origin, CH₄ may also have been brought by comets, cometsimals, and meteorites, especially because we are looking in craters (formed by impacts), and the impactors could have delivered both water and methane. Upon impact the material vaporizes and releases volatiles both from the impactor and from the lunar material. Although some of the gases may escape, others remain and can migrate to cold traps [Crider and Vondrak, 2000]. After a cometary impact, surface/subsurface CH₄ (Apollo samples containing CH₄ were taken from different depths) may become covered with water ice, since the impactor contained water ice, which has sublimed upon impact and redeposited (one of the factors in this process is the collision between particles after the impact).

Since methane on the Moon (at least part of it) is a soil chemistry product from the solar wind implanted H and C, it is constantly being replenished on the surface by the solar wind (a slow but steady source) and then buried deeper by meteoroid bombardment, including micrometeoroids, which constantly rework and mix the lunar soil; that is, lunar gardening occurs [Heiken *et al.*, 1991, pp. 45–47]. The CH₄ gas, buried under water ice (or permafrost), would diffuse into the water

ice and, under the stabilizing (T, P) conditions, which we have calculated to be possible on the Moon, would form clathrate. There were suggestions that some of the lunar volatiles on the surfaces of lunar soil grains might be of volcanic origin [Heiken *et al.*, 1991, pp. 311 and 315, and references therein]. Also, codeposition of CH₄ molecules and water ice molecules in near-vacuum conditions is possible.

For comparison at a higher temperature, methane hydrate is stable at $T = 148.8$ K under the partial pressure $P = 5.3 \times 10^3$ Pa [Falabella, 1975; Sloan, 1998, p. 315]. Under the assumption of minimum density (900 kg/m³ for water ice) this gives a depth h of ~ 3.3 m. (Not all of the upper layer has to be water ice or permafrost.) Since the triple point of methane is (90.7 K, 12,159 Pa) and, at an even higher temperature of 100 K, the methane gas partial pressure for the formation of this clathrate hydrate is only 2.1 Pa, methane clathrate hydrate is very stable relative to solid or liquid methane.

Carbon dioxide clathrate hydrate is stable at $T = 151.5$ K under the partial $P = 535$ Pa [Miller and Smythe, 1970; Sloan, 1998, p. 333]. Again, assuming the water-ice density, the minimum stability depth on the Moon for CO₂ · 6H₂O is calculated to be ~ 38 cm. Moreover, this holds for permafrost because it has a higher density.

Laboratory measurements of the kinetics of CO₂ clathrate formation by Saji *et al.* [1995] showed that the formation rate becomes lower with increasing pressure. This is important for the lunar case, where the stabilizing depth is small; thus shallow clathrate hydrate forms faster compared to the hydrate formation at greater depths.

If the surface temperature in lunar craters is lower than used in our calculations, then even less pressure is needed to stabilize clathrate hydrate, and hence they can exist at even shallower depths. In connection with the previous suggestions to use water ice deposits as a source of fuel, the possible near-surface methane clathrate hydrate deposits are even more useful. We underline that CH₄ · 6H₂O contains not only a fuel but oxygen in H₂O to burn the fuel. Moreover, CH₄ is the most efficient fuel, since the carbon in it is in the most reduced state.

The experiments by Ershov *et al.* [1991] showed that the (T, P) conditions from the stability diagram are necessary for the clathrate hydrate formation but not for its existence, if it has already been formed. This is due to the fact that upon the dissociation of the external layer of clathrate hydrate, water ice (the case when $T < 0^\circ\text{C}$) and gas are generated. The newly produced external layer of water ice seals and thermally insulates the clathrate hydrate and hydrate stabilizes [Sloan, 1998, p. 19].

Since seismic and electrical properties of methane clathrate hydrate and water ice are similar, standard geophysical methods are not applicable (including radar observations) to discriminate between those substances. We suggest an experiment for detecting subsurface clathrate hydrate by forced dissociation of the lunar material and then determination of the ratio and the composition of the released gases. In situ clathrate hydrate detection techniques can use the property that the thermal conductivity of methane clathrate hydrate is about five times lower than that of water ice.

We also propose observations to identify methane clathrate to be performed on the Moon by mounting a high-resolution spectrometer on a descent vehicle with a light source and then comparing the reflectance spectra. Since the clathrate can be stable only in the subsurface (though it may be very shallow from our model calculations), one has first to expose the clath-

rate (e.g., by an impact and the clathrate will begin to dissociate). The suggested near-IR region to distinguish between methane clathrate and water ice is at ~ 2.3 microns. These reflectance spectra are from the laboratory measurements of Smythe [1979, pp. 41–42, Figure VIa].

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